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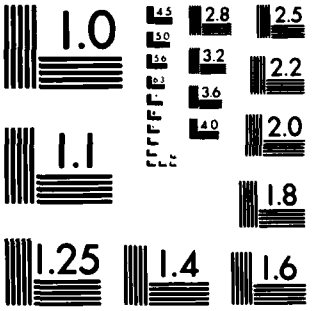

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Photolysis of aminocoumarin laser dyes, including 7-diethylamino-4-methylcoumarin has been investigated. Dealkylation of groups at the 7-dialkylamino functionality, reduction of the lactone moiety and overall photodecomposition of dyes have been observed. Concentration quenching of dye fluorescence is important at concentrations above 0.01 M. The photolysis is ascribed to singlet self quenching; triplet states are formed in low yield (flash photolysis) and are not reactive.

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# PHOTODEGRADATION OF COUMARIN LASER DYES. AN UNEXPECTED SINGLET SELF-QUENCHING MECHANISM

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Aminocoumarins are widely used in dye lasers for the blue-green region[2] despite problems of photodegradation[3] which reduce service life and lasing efficiency. A number of reports have recently appeared involving the characteristics of dye solutions under conditions of flash-lamp pumping[4] and the effects of additives which inhibit photodegradation.[5] We have investigated the mechanism of dye photodecomposition and wish to report here a number of unusual characteristics for three representative dyes.[6] In particular, the self-quenching of dye singlets remains deleterious despite the typically short singlet lifetimes and moderate dye concentrations. In addition, triplet photochemistry appears to be unimportant for direct photolysis of the coumarins,[7] and a well known electron transfer path involving tertiary amine moieties, which might have served as

a model for photodecomposition, is likewise unsuitable.

Lengthy irradiation of coumarins 1-3 (Hg lamps, Pyrex filter, argon purged solutions) results in loss of dye which can be followed spectrophotometrically. The filmy deposit which results is not readily characterized; nmr analysis of the progress of photolysis simply shows dye disappearance. For structures 1 and 2, gas chromatograms (2 m 10% OV-101 column, 200°) reveal small amounts of at least two products which grow to very modest levels (generally < 1%) and finally disappear. The monodealkylated coumarins 4[3a] and 5 as well as products of bis-dealkylation could be identified by comparison with authentic samples. Another product originating from 1 could not be isolated but was identified by glc-ms analysis as the reduced species 6.[8,9] Photodecomposition, including formation of 4 and 5, was observed in a variety of solvents including acetonitrile, toluene, chloroform, and cyclohexane. Comparable efficiencies were generally observed; degradation was somewhat enhanced in chloroform but retarded in alcohols.

The triplet of 1 can be observed as an absorbing transient by flash photolysis.[10] Addition of trans-stilbene (0.06 M) serves to effectively quench this triplet but does not inhibit the photodecomposition of 1 to 4 and 6. The triplet was observed (xenon flash lamp, pulse duration = ca. 30 μs FWHM, argon purge, $\lambda_{max}$ = 625 nm [10]) to undergo first order decay in acetonitrile which is dependent on [1]. The triplet self quenching data revealed a unimolecular decay constant of $2.4 \times 10^5 s^{-1}$ and a concentration quenching constant, $k = 1.3 \times 10^9 M^{-1}s^{-1}$, similar to the behavior of the triplet state of Michler's ketone ($k = 1.25 \times 10^9 M^{-1}s^{-1}$ in benzene).[11,12]

Anticipating a bimolecular singlet reaction, fluorescence quantum yields were measured as a function of dye concentration using the front-face illumination technique. Emission quenching was indeed readily observed in a relatively high concentration range (0.01-0.25 M) and analyzed according to the model shown below (Scheme), and the relationships among fluorescence yield ($\phi_f$), photoreaction yield ($\phi_r$), and dye concentration which are readily derived. Values for the sum of self-quenching constants, $k_{cq}$ and $k_r$ were calculated from the slopes of reciprocal quantum yield - concentration plots, and are shown in the Table along with fluorescence yield and lifetime data obtained for very dilute dye solutions ($\leq 10^{-4}$ M).[6a] The trends in rate of total self-quenching ($k_{cq} + k_r$) are modest but suggest a more favorable interaction between ground and excited state for dyes which support a larger dipole moment (2 and 3 over 1).

Scheme

$$D \xrightarrow{h\nu} D^*$$

$$D^* \longrightarrow D + h\nu \qquad k_f$$

$$D^* \longrightarrow D + \Delta \qquad k_d$$

$$D^* + D \longrightarrow 2D \qquad k_{cq}$$

$$D^* + D \longrightarrow \text{products} \qquad k_r$$

$$1/\phi_f = \frac{k_f + k_d}{k_f} + \frac{k_{cq} + k_r}{k_f}\,[D]$$

$$1/\phi_r = \frac{k_r + k_{cq}}{k_r} + \frac{k_d + k_f}{k_r}\,\frac{1}{[D]}$$

The photodegradation mechanism involving singlet self-quenching was fortified by measurement of the profile of quantum yield for conversion 1 → 6 as a function of [1] measured at very low conversion ( ≤ 0.01%). A double reciprocal plot provided an alternative source or the sum, $k_{cq} + k_r$ = $7.8 \times 10^8$ $M^{-1}s^{-1}$, a value in reasonable agreement[9] with the figure obtained for fluorescence quenching in acetonitrile (Table). The limiting quantum yield ($k_r/k_r + k_{cq}$) for formation of 6 was $3 \times 10^{-4}$ indicating that the dominant result of self quenching is return to ground state dye.

A reasonable mechanism which follows for dealkylation in polar media finds analogy in the bimolecular photochemistry of tertiary amine functions.[14] The steps would include for the present dyes electron transfer self-quenching, proton transfer leading to free α-aminoalkyl radicals (e.g., 7) which lose a second electron, followed by hydrolysis of a resulting iminium or enamine function. The data for 1 and 2 do not support such a mechanistic route for amine fragmentation. Added water does not alter significantly the course of phototolysis in acetonitrile (indeed, dealkylation occurs in all media), and acetaldehyde (expected from iminium hydrolysis[14a]) was not observed as a byproduct.[15] Dealkylation is in fact inhibited with added methyl viologen ($MV^{2+}$, 3.0mM) a well known electron transfer quencher,[16] even though flash photolysis of 1 (0.02 mM) and $MV^{2+}$ in argon-purged water results in formation of the reduced viologen radical ($\lambda_{max}$ = 395 and 600 nm, half life = a few milliseconds). In addition, electrooxidation of 1-3 is reversible in acetonitrile,[17] suggesting that successive electron and proton transfer processes which irreversibly destroy the dyes are not efficient processes.

We favor a mechanism involving radicals, 7 and 8 as suggested by von Trebra and Koch.[5a] The origin of these species is a relatively slow and inefficient hydrogen atom transfer step,[18] occurring within a singlet excimer intermediate obtained on dye self quenching. Reduction product 6 results from disproportionation of 8, while 7 is permitted to participate in dealkylation or the induction of polymerization. Free radicals are not readily observed due to fast in-cage reaction of singlet radical pairs (most returning to native dye) which may include coupling to form aminol derivatives capable of rearrangement finally leading to dealkylation and other products.[19]

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7. For an example of rhodamine laser dye photochemistry involving bimolecular triplet reaction, see Korobov, V.E.; Shubin, V.V.; Chibisov, A.K. Chem. Phys. Lett., 1977, 45, 498.

8. Major ms peaks for 6 were as follows: m/e = 233 (mol. ion), 218 ($-CH_3$), 190 ($-CH_3$, -CO or $C_2H_4$), 148 (190 - $CH_2CO$). A product having m/e = 205 (mol. ion) corresponding to hydrogenated 4 was also

observed in trace amounts.

9. The formation of trace products as determined by glc analysis displayed erratic behavior at longer irradiation times. At the shortest times suitable for product detection, 6 was favored over 4 by ca. 5:1 whereas this ratio was nearly reversed at intermediate irradiation periods.

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12. In a polar medium the yield of triplet 1 is clearly low (est. < 0.004[10]). Using 1,3-cyclohexadiene as a triplet counter,[13] we obtain a value for triplet formation of 0.006 for 1 (ethanol) and < 0.001 for 2 and 3.

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15. Added acetaldehyde survived irradiation and did not quench dye photolysis.

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17. Oxidation in acetonitrile gave half wave potentials of 1.09, 1.20, and 0.89 V vs SCE (all quasi-reversible waves) from cyclic voltammetry. Reduction values were -2.2, -1.7, and - 1.8 V (peak potentials, waves irreversible). Using singlet energies of 72, 64, and 61 kcal/mol for 1-3, the free energy change for dye self quenching via electron transfer can be calculated ($\Delta G$ = 0 - 5 kcal/mol).

18. In-cage successive electron-proton transfer leading to 7 and 8 cannot be ruled out (note energetics[17]).

19. a. A role for radicals which reach bulk solution is clearly indicated by the inhibition of photolysis by thiols/sulfides (including incorporation of isotopic label in dye)[5a] and the amine DABCO.[5b] However, since monomeric or even dimeric products do not accumulate appreciably, the exact course of secondary steps is difficult to determine. An aminol coupling product has been proposed for the decomposition of Michler's ketone, by itself[20] and on reaction with benzophenone,[21] and appearance of the requisite radicals is indicated in flash photolysis results.[11,21]

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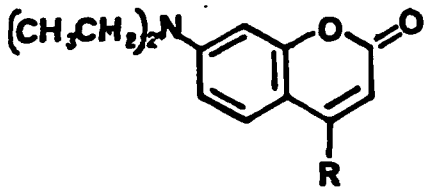
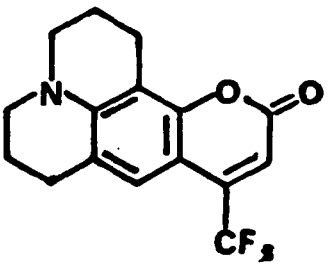
22. We thank Dr. A.N. Fletcher for correspondence concerning correction for oxygen quenching of dye fluorescence and for sending results prior to publication.



**1**, R=CH$_3$

**2**, R=CF$_3$



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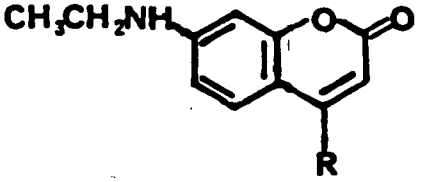
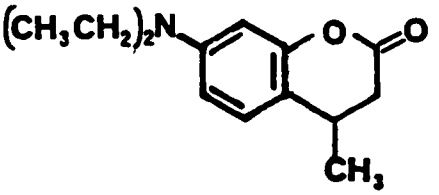
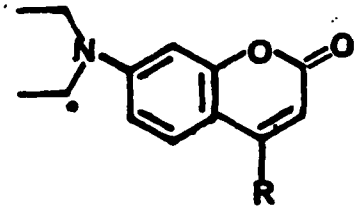


**4**, R=CH$_3$

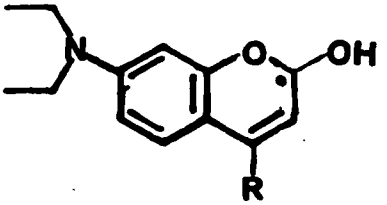
**5**, R=CF$_3$



**6**



**7**



**8**

Table. Photophysical Properties and Singlet Self Quenching Rate Data for Coumarin Dyes[a]

| Dye | Solvent | $\lambda_f$ (nm) | $\phi_f$ | $\tau_f$ (ns)[b] | $k_{cq} + k_r$ (X $10^{-9} M^{-1} s^{-1}$) |
|---|---|---|---|---|---|
| 1 | $CHCL_3$ | 421 | 1.01 | (3.1) | 1.1 |
| | $CH_3CN$ | 434 | 1.03 | 3.4 | 2.9 |
| | $CH_3CH_2OH$ | 451 | 0.73 | 3.1 | 4.5 |
| 2 | $CHCl_3$ | 466 | 0.92 | (4.6) | 5.3 |
| | $CH_3CN$ | 501 | 0.064 | 0.6 | 3.3 |
| | $CH_3CH_2OH$ | 509 | 0.078 | 0.8 | 14.7 |
| 3 | $CHCl_3$ | 483 | 0.80 | (5.4) | 3.5 |
| | $CH_3CN$ | 521 | 0.56 | 5.6 | 17. |
| | $CH_3CH_2OH$ | 531 | 0.38 | 3.4 | 6.9 |

[a]Fluorescence yield and lifetime data for acetonitrile and ethanol taken from ref 6.[22]

[b]Lifetimes in chloroform assumed similar to values measured for ethyl acetate solvent (ref 6).

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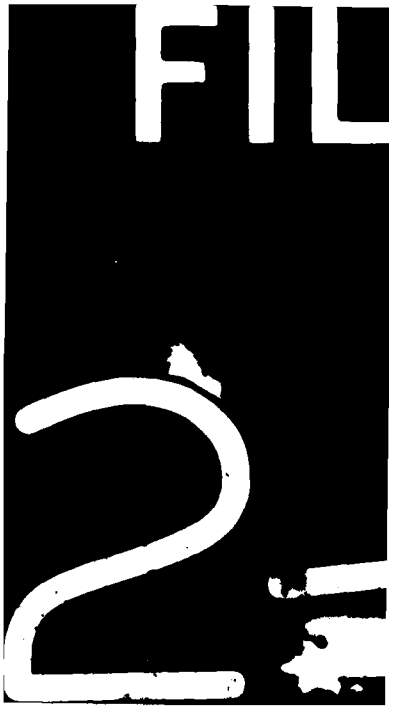
## ABSTRACT

The photolysis of a series of aminocoumarin laser dyes, including 7-diethylamino-4-methylcoumarin (1), has been investigated. Dealkylation of groups at the 7-dialkylamino functionality, reduction of the lactone moiety and overall photodecomposition of dyes have been observed. Concentration quenching of dye fluorescence is important at concentrations above 0.01 M. The concentration dependence of photoreduction is shown to be consistent with a singlet self-quenching mechanism. Dye photodegradation is not quenched on addition of trans stilbene, although the latter is an effective quencher of the triplet of 1. Intersystem crossing yields for the coumarin dyes are very low. A mechanism for dye photodegradation is proposed involving singled self-quenching, net hydrogen atom transfer between dye molecules, followed by disproportionation and coupling of radicals.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